Uniaxial-Pressure induced Ferromagnetism of Enhanced Paramagnetic $Sr_3Ru_2O_7$

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(Received February 2, 2008)

We report a uniaxial pressure-dependence of magnetism in layered perovskite strontium ruthenate $Sr_3Ru_2O_7$. By applying a relatively small uniaxial pressure, greater than 0.1 GPa normal to the RuO_2 layer, ferromagnetic ordering manifests below 80 K from the enhanced-paramagnet. Magnetization at 1 kOe and 2 K becomes 100 times larger than that under ambient condition. Uniaxial pressure dependence of Curie temperature T_C suggests the first order magnetic transition. Origin of this uniaxial-pressure induced ferromagnetism is discussed in terms of the rotation of RuO_6 octahedra within the RuO_2 plane.

KEYWORDS: $Sr_3Ru_2O_7$, Sr_2RuO_4, ferromagnetism, uniaxial pressure, nearly ferromagnetic metal, magnetization, structural distortion

§1. Introduction

Tuning the magnetism in solid state compounds via tiny perturbation is one of the central issues for strongly-correlated electron systems such as heavy-fermion (HF) intermetallic compounds. Since those materials tend to reveal the high susceptibility of the electronic properties to relatively small external pressures ($\leq$ GPa). For instance, antiferromagnetic HF compounds ($CeCu_2Ge_2$,[1)] $CeRh_2Si_2$,[2)] $CePd_2Si_2$[3)]) and a ferromagnetic HF compound (UGe_2[4)]) reveal superconductivity under several GPa hydrostatic pressures, which reduce the magnetic ordering temperature towards absolute zero. Around the diminishing region, the superconductivity appears. Several GPa pressures, which is necessary to induce the superconductivity in above HF compounds, are relatively small

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for solid considering that much more pressures are probably required to suppress ferromagnetic ordering temperatures above 600 K completely in conventional ferromagnets like Fe. In fact, under hydrostatic pressure, ferromagnetic Fe undergoes a structural phase transition at around 10 GPa. Below 10 GPa, ferromagnetic phase remains without showing large reduction of the ferromagnetic transition temperature.[5–7] Concerning pressure induced magnetism from paramagnetism, Umeo *et al.* reported that uniaxial pressure induced antiferromagnetism in CeNiSn (paramagnetic at ambient) above 0.1 GPa at 6 K.[8]

In the present study, we report a uniaxial pressure induced paramagnetic to ferromagnetic transition in two-dimensional (2D) ruthenium oxides (ruthenates) $Sr_3Ru_2O_7$ characterized by a paramagnetic state at ambient pressure.[9] Hydrostatic pressure is not vital to this transition as described later. Ruddelsden-Popper type ruthenates $A_{n+1}Ru_nO_{3n+1}$ (A: divalent alkali metal such as Sr and Ca, n = 1, 2, 3 and infinity) exhibit rich and comprehensive electronic ground states. The spin-triplet superconductor,[10–12] ferromagnetic metal,[13] antiferromagnetic Mott insulator[14] and antiferromagnetic metal[15] have been investigated extensively. $Sr_3Ru_2O_7$, which has a 2D crystal structure (Fig.1), is another such compound.[16–20]

The first report on single crystals grown via a floating-zone method indicated that $Sr_3Ru_2O_7$ is a paramagnet that exhibits enormously strong ferromagnetic instability, which is most consistent with the results of polycrystals.[16,17,19] Temperature dependence of magnetic susceptibility $\chi(T)$ is nearly isotropic and obeys Curie-Weiss law with antiferromagnetic Weiss temperature above 200 K. At around 17 K, $\chi(T)$ shows a broad maximum which is often observed in nearly ferromagnetic (enhanced paramagnetic) metal like Pd or $TiBe_2$. Below 7 K, temperature independent $\chi(T)$ and T-square behavior of in-plane and out of plane resistivities are recognized, indicating the Fermi liquid state with large Wilson ratio $R_W \geq 10$. Field dependence of magnetization $M(H)$ below 17 K reveals metamagnetic transitions around 50 kOe for $H||ab$ and 80 kOe for $H||c$. High purity single crystalline $Sr_3Ru_2O_7$ with in-plane residual resistivity of 0.8 $\mu\Omega$ cm does not exhibit superconductivity down to 200 mK. Very recently, Grigera *et al.* have reported the possibility of quantum critical phenomena at metamagnetic transition in $Sr_3Ru_2O_7$.[21] The quantum criticality around the expected critical point corresponding to the first-order metamagnetic transition is probably related to the strong ferromagnetic instability.[22–24] Several materials exhibiting strong ferromagnetic instability are recognized as being nearly ferromagnetic paramagnets. However, $Sr_3Ru_2O_7$ is the only compound of the nearly ferromagnetic paramagnet with 2D crystal structure.

In order to amplify the ferromagnetic instability in $Sr_3Ru_2O_7$, we performed magnetization measurements under hydrostatic pressure and observed the sign of ferromagnetic ordering at approximately 1 GPa.[9] However, improved technique proved that hydrostatic pressures up to 1.4 GPa do not induce magnetic ordering.[25] Therefore, considering the possibility of a pressure component that

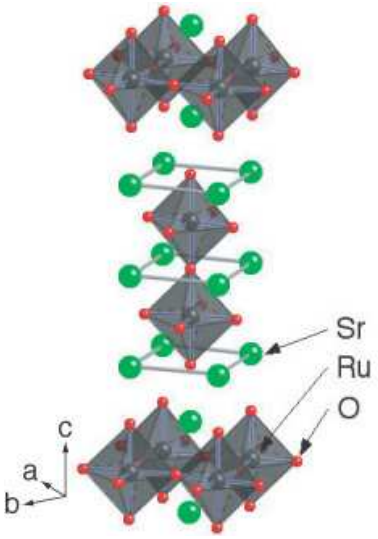

Fig. 1. Crystal structure of bilayered strontium ruthenate $Sr_3Ru_2O_7$. Strontium and ruthenium ions are positioned at tetragonal symmetry sites characterized by the space group of I4/mmm, which is the same as that of superconducting single-layered Sr_2RuO_4. SrO rock-salt layers and RuO_2 layers are alternately stacked forming a typical layered perovskite structure with RuO_6 octahedra. Each RuO_6 octahedron shares its oxygens at the corner. Considering oxygen ions, the symmetry is lowered to orthorhombic space group of *Bbcb* due to the RuO_6 rotation by about 7 degrees. The c-axis is normal to the two-dimensional RuO_2 planes.

is uniaxial with respect to the ferromagnetism, we performed uniaxial pressure measurements on single-crystalline $Sr_3Ru_2O_7$ for the first time. Uniaxial pressure was found to induce paramagnetic-to-ferromagnetic transition at pressures over 0.1 GPa, which, for inorganic materials, is a rather low critical pressure.

§2. Experimental method

Single crystalline $Sr_3Ru_2O_7$ was grown using a typical floating-zone technique.[26] Magnetization measurements under uniaxial pressure were performed by SQUID (superconducting quantum interference device) magnetometer. The uniaxial pressure ($p \leq 0.5$ GPa) and magnetic field ($H \leq 55$ kOe) were applied along the normal axis (c-axis) to the 2D RuO_2 plane in $Sr_3Ru_2O_7$. The pressure is estimated based on the shift of the superconducting transition temperature T_c of Sn.[27]

§3. Results and Discussion

Figure 2 illustrates the field-dependent magnetization $M(H)$ for several uniaxial pressures up to approximately 0.5 GPa at 2 K. Linear field dependence is observed for ambient atmospheric

conditions (i.e. uniaxial pressure $p = 0$ GPa), which is consistent with paramagnetic behavior.

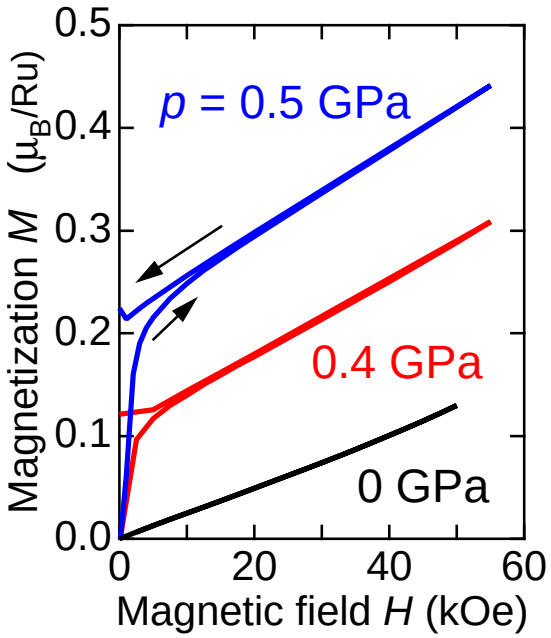

Fig. 2. Magnetic field dependence of magnetization $M(H)$ of single-crystalline $Sr_3Ru_2O_7$ at the temperature of 2 K. Magnetic field and uniaxial pressure are applied along the c-axis. Uniaxial pressure above 0.1 GPa causes ferromagnetic phase from paramagnet. The observed linear field dependent $M(H)$ reflects paramagnetic phase at $p = 0$ GPa. Increasing pressure leads to a larger remanent magnetic moment at zero field. The hysteresis curves, which do not saturate at the field of 55 kOe, are typical for metallic magnetism with a ferromagnetic component below the saturation field.

At $p \geq 0.1$ GPa, ferromagnetic characteristics appear unexpectedly in the magnetization curve $M(H)$, indicating pressure-induced ferromagnetic transition from the paramagnet phase. With pressures increasing beyond this critical value, the magnetization is enhanced. At $p = 0.5$ GPa and H=55 kOe, magnetization reaches almost 0.5 μ_B/Ru. In addition, no saturation behavior is observed at higher fields. This type of non-saturated feature is typical for metallic ferromagnets such as $SrRuO_3$ under the magnetic field smaller than the saturation field.[28)]

Assuming fully localized 4d electron in Ru ion sites (Ru^{4+}) and a stronger crystalline electrical field than spin-orbit coupling, four 4d electrons are distributed in three t_{2g} orbitals (d_{xy}, d_{yz}, d_{zx}), resulting in spin quantum number of S=1, corresponding to $2\mu_B$/Ru. If the uniaxial pressure-induced ferromagnetic transition in the present study is canted antiferromagnetic, the canting

angle of Ru spins should be greater than 14 degrees in the case of completely localized electron phases. Such a localized system implies the insulating conductivity phase known as a Mott insulator. Electrical resistivity measurements under uniaxial pressure along c-axis in $Sr_3Ru_2O_7$ up to a pressure of 0.1 GPa imply that there is no metal-insulator transition.[29] This indicates that uniaxial pressure-induced ferromagnetic transition does not concur with charge transport transition.

In the uniaxial pressure-induced magnetic phase, S can not easily be assumed to be approximately 1. In itinerant electron systems, S is much smaller than that in the localized case. Hence, the canted antiferromagnetic phase in $Sr_3Ru_2O_7$ is possible only when the canting angle of Ru-spins is much greater than 14 degrees. It is appropriate to assume a finite spin-orbit $(L-S)$ coupling in these ruthenates due to the large mass of Ru ions. In such a case, structural modifications are related to the spin canting angle. Huang *et al.* and Shaked *et al.* reported that the RuO_6 octahedron in $Sr_3Ru_2O_7$ rotates about the c-axis by 7 degrees.[30,31] Other structural strains, such as tilting from the 2D plane, were not detected. If the rotation angle matches the spin canting angle due to the finite $L-S$ coupling, the spin canting in the uniaxial-pressure-induced magnetic phase in $Sr_3Ru_2O_7$ exists within the 2D RuO_2 plane and its angle is approximately 7 degrees. However, the canting angle of 7 degrees within the RuO_2 plane can not explain the large moment of approximately 0.5 μ_B/Ru in the metallic phase as discussed above. In addition, spin canting within the 2D plane cannot induce a ferromagnetic moment along the c-axis in this crystal structure. Therefore, the observed pressure-induced ferromagnetic phase is thought to have originated from a simple ferromagnetic alignment of Ru spins.

The temperature dependence of magnetization $M(T)$ for various uniaxial pressures is shown in Fig.3. Data for both field-cooling sequences and zero field-cooling sequences is presented. Above 0.1 GPa, considerable abrupt magnetization develops at around 80 K. Increasing the pressure, the magnetic moment at 2 K becomes larger without changing ferromagnetic ordering temperatures T_c. The magnetization at approximately 0.5 GPa in $Sr_3Ru_2O_7$ is 100 times greater than that at ambient pressure. Releasing the pressure to zero, $M(H)$ and $M(T)$ again become paramagnetic, indicating good reproducibility. This enormous uniaxial pressure effect suggests that $Sr_3Ru_2O_7$ exhibits $piezo-ferromagnetism$, which means uniaxial- pressure induced ferromagnetism, perhaps due to the change in crystal structure explained below. Concerning the uniaxial pressure dependence of T_c, it seems that the first order transition driven by the pressure is accompanied by the appearance of the ferromagnetism.

In order to understand this outstanding instability of magnetism to small uniaxial pressure, we focus on the RuO_6 rotation angle in $Sr_3Ru_2O_7$. The significance of the RuO_6 rotation is evident since the observed variation in the rotation angle with decreasing temperature in $Sr_3Ru_2O_7$ is quite large (≈ 15 %) in comparison with the case of other lattice parameters (≤ 1 %).[31] On the contrary,

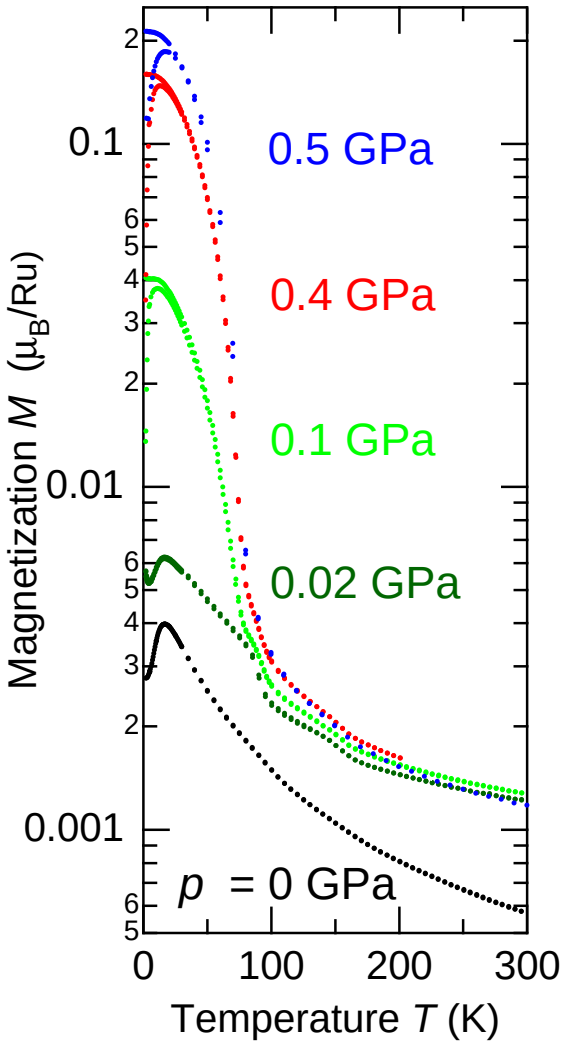

Fig. 3. Temperature dependence of magnetization $M(T)$ of single-crystalline $Sr_3Ru_2O_7$ for each uniaxial pressure at the field of 1 kOe. Magnetic field and uniaxial pressure are applied along the c-axis. Anomalous evolution of ferromagnetism with increasing uniaxial pressure is shown using a semilogarithmic scale. The ferromagnetic transition temperature T_c remains constant with varying the uniaxial pressure.

hydrostatic pressure, which is not essential for the above induced-ferromagnetism, does not modify the RuO_6 rotation angle.[31] In 2D R-P ruthenates, the rotation angle is vital in determining the electronic states.[32,33] For instance, a similar situation is realized in the surface state of Sr_2RuO_4, whereby the RuO_6 octahedron also rotates by 7 degrees, as is the case in bulk state $Sr_3Ru_2O_7$. Surface ferromagnetism caused by the rotation was theoretically derived.[34] Furthermore, consid-

ering other precious metal oxides, IrO_6 octahedra in layered perovskites Sr_2IrO_4 and $Sr_3Ir_2O_7$ also rotate along the direction normal to the 2D plane.[35–38] This type of structural distortion generally dominates the electronic state in layered perovskite maerials, by tuning electron transfer within the 2D plane. For instance, both iridates above are ferromagnetic semiconductors reflecting the stronger effective correlation. On the other hand, Sr_2RuO_4 and Sr_2MoO_4, which have no such structural distortions, are Pauli paramagnetic conductors.[39–41]

Therefore, we regard the rotation angle as an indicator of the uniaxial-pressure-induced ferromagnetism. Our calculations based on the 2D three-band Hubbard model with the RuO_6 octahedron rotation suggest that the quantum phase transition toward the ferromagnetic phase from quantum disordered state ($p = 0$ GPa) due to Ru-4d orbital degeneracy can occur by small changes in the RuO_6 rotation angle in $Sr_3Ru_2O_7$.[42] These calculation results and the existence of the same structural distortions in layered perovskite precious metal oxides may assure that the rotation angle of RuO_6 octahedra is the clue to understand the pressure-induced ferromagnetism in $Sr_3Ru_2O_7$. It is strongly required to perform the neutron diffraction measurements under the uniaxial pressure to determine the relation between structural distortions and magnetism on single crystalline $Sr_3Ru_2O_7$.

§4. Conclusion

In conclusion, we have reported the observation of remarkable uniaxial-pressure-induced ferromagnetic transition from the enhanced paramagnetic state in $Sr_3Ru_2O_7$. The uniaxial pressure dependence of T_c indicates that the appearance of ferromagnetism is corresponding to the first order phase transition driven by the pressure. In addition, $Sr_3Ru_2O_7$ is the candidate for the practical $piezo - ferromagnet$ due to its rather small critical pressure. The origin of appearance of the ferromagnetism is probably associated with the change in RuO_6 rotation angle, suggesting a possible criterion which may be used to find further examples of practical $piezo - ferromagnet$ candidates with higher critical temperatures.

Acknowledgements

The authors would like to thank H. Eisaki, A.P. Mackenzie, I. Nagai, Y.Maeno, M.K. Crawford, M. Takigawa, C.H.Lee and J. Itoh for their helpful advice and kind assistance. This study was supported in part by a Grant-in-Aid for the Scientific Research on Priority Area "Novel Quantum Phenomena in Transition Metal Oxides" from the Ministry of Education, Culture, Sports, Science and Technology.

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